

BUREAU OF MINES INFORMATION CIRCULAR/1994



The Materials Flow of Arsenic in the United States

By J. Roger Loebenstein

UNITED STATES DEPARTMENT OF THE INTERIOR

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Information Circular 9382

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UNITED STATES DEPARTMENT OF THE INTERIOR Bruce Babbitt, Secretary

BUREAU OF MINES

Library of Congress Cataloging in Publication Data:

Loebenstein, J. Roger.

The materials flow of arsenic in the United States / by J. Roger Loebenstein.

p. cm. — (Information circular, 9382)

Includes bibliographical references (p. 10).

1. Arsenic wastes—Environmental aspects—United States. 2. Arsenic industry—United States. I. Title. II. Series: Information circular (United States. Bureau of Mines); 9382.

TN295.U4 [HD9539.A943U6] 622 s—dc20 [363.73'84] 93-42629 CIP

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

h/d hour per day

mt metric ton

d/yr day per year

mt/yr metric ton per year

kg kilogram

% percent

lb pound

THE MATERIALS FLOW OF ARSENIC IN THE UNITED STATES

By J. Roger Loebenstein¹

ABSTRACT

This report presents a U.S. Bureau of Mines study of the flow of arsenic-containing materials in the United States, based on the best data available in 1991. It includes a consideration of arsenic as a byproduct of the processing of nonferrous metals, the fate of arsenic in manufacturing wastes, the quantity of arsenic used in products, the fate of arsenic in dissipative uses, and the useful life of discarded products. Where possible, estimates are given of the amounts of arsenic lost from the materials flow.

Arsenic is a byproduct of mining nonferrous metals. Historically, most U.S. production has been from the states of Montana, Washington, and Utah. The smelters in these states are believed to be the areas of the country where arsenic is most concentrated in the soil, tailings ponds, and waste dumps. Since the closure of the last domestic producer of arsenic in 1985, all arsenic has been derived from imported sources.

Historically, arsenic was important in agricultural applications as an insecticide, herbicide, and cotton desiccant. As the environmental movement gained momentum and the toxicity of arsenic became better understood, most of the agricultural uses for arsenic were banned. Beginning about 1975, the use of arsenic as a wood preservative began to grow. After 1980, wood preservative uses became more important than agricultural applications. By 1990, 70% of the arsenic consumed in the United States was used by the wood preservative industry and 20% by the agricultural industry.

The major source of domestic arsenic emissions in 1989 was from the U.S. copper processing industry. About 7,800 mt/yr of arsenic was discarded in leach dumps, tailings, and slag. Another 800 mt/yr was liberated to the atmosphere and 1,400 mt/yr was exported in copper concentrates. On the consumption side, 9,200 mt/yr was lost, mostly from dissipative agricultural uses and the disposal of obsolete arsenical products.

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INTRODUCTION

The U.S. Bureau of Mines has initiated a series of studies on the flow of mineral commodities from mine through end use. This paper is primarily concerned with tracing the flow of arsenic in the United States. All figures shown are in terms of metric tons of contained arsenic, although arsenic trioxide, As₂O₃, or white arsenic, is the most important commercial product.

The toxic effects of arsenic have been known for centuries. There are many different arsenic compounds in the environment: hydrides, oxides, sulfides, arsenites, arsenates, and organic arsenic compounds. In general, inorganic arsenic compounds are considered to be more toxic than organic compounds. Arsine (AsH₃) and arsenic (III) halogenides are more toxic than other inorganic arsenic compounds.

Global emissions of arsenic from the smelting of metals, the burning of coal, and industrial uses have been estimated at 24,000 mt/yr up to as high as 124,000 mt/yr. This compares with natural releases, mostly from volcanoes, ranging from 2,800 mt/yr to 8,000 mt/yr (1).² Thus, mining and industrial releases of arsenic are roughly 10 times greater than natural releases.

The presence of arsenic in nonferrous metal ores has commonly been viewed as a problem, not a benefit. Because of the toxicity of arsenic, its relatively low price, and environmental problems associated with its production, domestic smelters today may choose to discard arsenic rather than produce it.

HISTORICAL PRODUCTION

In the early part of the century, as today, most arsenic was a byproduct of mining other metals. Arsenic trioxide was first produced in the United States as a byproduct of smelting gold and silver ores at Everett, WA, in 1901 (2). In the early part of the century, most production was from Montana and Utah. In 1917, for example, Butte, MT, and the Tintic district, UT, were important sources of arsenical ores. About 14,000 mt of arsenic trioxide (10,600 mt arsenic content) was liberated each year to the atmosphere from smelting the ores from these two sites alone (3). In 1944, when production peaked, producers of arsenic included the American Smelting and Refining Co., Anaconda Copper Mining Co., Ferro-Enamel Corp. and Ferro Enamel Supply Co. (calcium arsenate), Jardine Mining Co., Shepherd Chemical Co. (sodium arsenite), and the United States Smelting, Refining & Mining Co. (4). By 1960, the entire U.S. production of arsenic was a byproduct of smelting arsenical copper and lead ores at the Anaconda, MT, smelter of the Anaconda Company and the Tacoma, WA, smelter of the American Smelting and Refining Company (5).

Most domestic arsenic was produced as the trioxide (As₂O₃), which was recovered from flue dusts, speiss,³ and sludges associated with the smelting of copper, lead, gold, and silver ores that contained arsenic. The arsenic trioxide formed during the smelting process volatilized and was concentrated principally in the flue dust. Arsenic trioxide of commercial purity was obtained by stepwise distillation from the flue dust.

Table 1 lists copper and lead smelter locations where arsenic was recovered for sale between 1910 and 1985, after which all domestic production of arsenic ceased. These and other similar smelter sites are places where arsenic is concentrated in the soil, tailings ponds, and waste dumps (6).

Domestic arsenic production peaked at 24,878 mt in 1944, and was terminated in 1985 when ASARCO Incorporated, the sole remaining producer, closed its copper smelter and associated arsenic recovery plant in Tacoma, WA. The projected high cost of bringing the old smelter into compliance with Federal, State, and local regulations on atmospheric emissions of sulfur dioxide principally and, to a lesser extent, arsenic, was part of the reason for the closing. As shown in table 2, imports have replaced domestic production in supplying consumers.

Table 1.—U.S. smelters producing arsenic for sale, 1910-85

Location	Years in operation
Anaconda, MT	1910 to 1965
Brinton, VA	1917 to 1918
Denver, CO	1910 to 1931
El Paso, TX	1938 to 1949
Everett, WA	1910 to 1916
Jardine, MT	1923 to 1925, 1932 to 1936
Martinez, CA	1924
Midvale, UT	1919 to 1959
Murray, UT	1926 to 1938, 1943 to 1952
Perth Amboy, NJ	1920 to 1925
Pittsburg, CA	1923
Tacoma, WA	1917 to 1985
Tooele, UT	1921 to 1923
Toulon, NV	1923 to 1924

Source: Arsenic chapters in USBM Minerals Yearbooks.

²Italic numbers in parentheses refer to items in the list of references preceding the appendix at the end of this report.

³Metallic arsenides and antimonides smelted from cobalt and lead ores.

Table 2.—Arsenic supply-demand relationships, 1910-90

(Metric tons, arsenic content)

1910	1920	1930	1940	1950	1960	1970	1980	1990
								,
	7,899	11,966		•			•	-
926	2,568	7,191	6,819	10,146	9,000	13,500	9,100	20,693
NA	NA	NA	NA	NA	700	5,800	_	100
1,954	10,467	19,157	22,847	22,047	19,100	29,200	12,500	20,793
NA	NA	NA	NA	NA	2,400	10,800	100	100
_	,	· NA	1,487	_	_	_	-	149
1,954	10,467	19,157	21,360	22,047	16,700	18,400	12,400	20,544
NA	- NA	13,400	20,100	12,000	12,300	14,600	5,700	4,200
NA.	NA	1,000	600	NA	1,800	1,900	600	800
NA	· NA	3,600	400	NA	1,600	900	5,400	14,400
NA	NA	NA	NA	NA	500	500	400	800
NA	NA	1,157	260	NA	500	500	300	300
1,954	10,467	19,157	21,360	22,047	16,700	18,400	12,400	20,500
	1,028 926 NA 1,954 NA — 1,954 NA NA NA NA	1,028 7,899 926 2,568 NA NA 1,954 10,467 NA NA 1,954 10,467 NA	1,028 7,899 11,966 926 2,568 7,191 NA NA NA 1,954 10,467 19,157 NA NA NA 1,954 10,467 19,157 NA NA 13,400 NA NA 13,600 NA	1,028 7,899 11,966 16,028 926 2,568 7,191 6,819 NA NA NA NA 1,954 10,467 19,157 22,847 NA NA NA NA NA NA 1,487 1,954 10,467 19,157 21,360 NA NA NA 13,400 20,100 NA NA NA 1,000 600 NA NA NA 3,600 400 NA	1,028 7,899 11,966 16,028 11,901 926 2,568 7,191 6,819 10,146 NA NA NA NA NA 1,954 10,467 19,157 22,847 22,047 NA NA NA NA NA NA - NA NA 1,487 - 1,954 10,467 19,157 21,360 22,047 NA NA NA 13,400 20,100 12,000 NA NA NA 1,000 600 NA	1,028 7,899 11,966 16,028 11,901 9,400 926 2,568 7,191 6,819 10,146 9,000 NA NA NA NA NA NA NA NA 700 1,954 10,467 19,157 22,847 22,047 19,100 NA NA NA NA NA NA 2,400 NA NA NA NA NA NA 2,400 NA NA 13,400 20,100 12,000 12,300 NA NA NA 1,000 600 NA 1,800 NA NA NA NA NA NA NA 1,600 NA NA NA NA NA NA NA 500 NA NA NA NA NA NA S00 NA NA NA 1,157 260 NA 500	1,028 7,899 11,966 16,028 11,901 9,400 9,900 926 2,568 7,191 6,819 10,146 9,000 13,500 NA NA NA NA NA NA NA TOO 5,800 1,954 10,467 19,157 22,847 22,047 19,100 29,200 NA NA NA NA NA NA NA 2,400 10,800 NA NA NA 1,487 — — — 1,954 10,467 19,157 21,360 22,047 16,700 18,400 NA NA 13,400 20,100 12,000 12,300 14,600 NA NA NA 1,000 600 NA 1,800 1,900 NA NA NA 3,600 400 NA 1,600 900 NA NA NA NA NA NA NA NA SOO 500 NA NA NA NA NA NA NA SOO 500	1,028 7,899 11,966 16,028 11,901 9,400 9,900 3,400 926 2,568 7,191 6,819 10,146 9,000 13,500 9,100 NA NA NA NA NA NA NA TOO 5,800 — 1,954 10,467 19,157 22,847 22,047 19,100 29,200 12,500 NA NA NA NA NA NA NA 2,400 10,800 100 — NA 1,487 — — — — — 1,954 10,467 19,157 21,360 22,047 16,700 18,400 12,400 NA NA 13,400 20,100 12,000 12,300 14,600 5,700 NA NA NA 1,000 600 NA 1,800 1,900 600 NA NA NA 3,600 400 NA 1,600 900 5,400 NA NA NA NA NA NA NA NA SOO 500 400 NA NA NA NA NA NA NA SOO 500 300

NA Not available.

¹Shipments were used instead of production in 1930, 1940, and 1950.

²Calculated as refinery production plus imports plus industry beginning stocks less industry ending stocks less exports.

Sources: Arsenic ch. in USBM Minerals Yearbook, 1930, 1940, 1950, 1960, and 1991 eds. U.S. Bureau of Mines Commodity Statement, 1969 ed. Arsenic ch. in USBM Mineral Facts and Problems, 1975 and 1985 eds. Mineral Industry Surveys, Annual Review, Arsenic, 1991.

Figures for domestic arsenic supply and demand from 1910 to 1990 are shown in 10-year increments in table 2. Figures for domestic production of arsenic trioxide from 1910 to 1959 were published in the 1960 edition of Bureau of Mines Minerals Yearbook chapter on arsenic. Figures for later years are available from Minerals Yearbook chapters and from Mineral Facts and Problems, 1980 and 1985

editions. The most recent information on arsenic is published in the Mineral Industry Surveys annual reviews of arsenic. The arsenic content of arsenic trioxide was calculated as 75.7% of trioxide weight. Unless otherwise stated, all figures in this paper are in terms of arsenic content.

LEGISLATIVE REGULATION

Most of the published literature on arsenic emissions dates back to the mid-1970's, when the Environmental Protection Agency (EPA) studied the domestic nonferrous emelting industry and the associated arsenic extraction industry in depth. In 1978, the U.S. Occupational Safety and Health Administration (OSHA), having concluded that inorganic arsenic is a carcinogen and that worker exposure to it must be limited, promulgated its final standard on occupational exposure to inorganic arsenic. Two years later, EPA listed inorganic arsenic as a hazardous air pollutant, based on its findings that inorganic arsenic is carcinogenic to humans and that there was significant public exposure to the pollutant. In 1983, the agency estimated that more than 85% of the 1,200 tons per year of atmospheric arsenic emissions came from copper smelters and glass manufacturing plants (7).

The largest contributor to arsenic emissions, a smelter in Tacoma, WA, predominantly processed imported high-arsenic copper concentrates. With the closure of this smelter in 1985, high-arsenic concentrates were no longer imported. Fourteen low-arsenic feed copper smelters were operating in 1983, located predominantly in the far South-west. Seven of the smelters were in Arizona, two in New Mexico, and one each in Michigan, Nevada, Tennessee, Texas, and Utah. The glass manufacturing plants were in the states of Indiana, Kentucky, Ohio, Rhode Island, Louisiana, Pennsylvania, New York, and West Virginia.

In 1983, EPA also identified other arsenic source categories for which standards were not proposed at that time: primary lead and zinc smelters, zinc oxide plants, arsenic chemical manufacturing plants, cotton gins, and secondary lead smelters (8). By 1986, the agency had

³Distribution of demand pattern is based on text of Minerals Yearbook chapters in 1930 and 1940. Figure for wood preservatives in 1930 includes some arsenic weed killer that should be included in the agricultural chemical category. Agricultural chemical figure for 1950 represents the arsenic content of lead arsenate and calcium arsenate produced. Total demand for 1990 was rounded.

issued its final rules on arsenic emissions from copper smelters and glass-manufacturing plants.

EPA also regulates the uses of inorganic arsenic under provisions of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (9). A pesticide product may be sold or distributed in the United States only if it is registered with EPA or exempt from registration under FIFRA. Before a product can be registered as a pesticide, it must be shown that it can be used without "unreasonable

adverse effects on the environment," and without causing "any unreasonable risk to man and the environment taking into account the economic, social and environmental costs and benefits of the use of the pesticide." It is the responsibility of the proponent of initial or continued registration to prove that the pesticide meets the risk and benefit standard of FIFRA. If at any time EPA determines that a pesticide does not meet this standard, it may cancel the registration under Section 6 of FIFRA.

HISTORICAL USES

The estimated U.S. demand pattern for arsenic is shown in table 2 in 10-year increments from 1910 to 1990. While the breakdown of demand for 1910 and 1920 was not available, most arsenic was used in those years by manufacturers of insecticides, particularly calcium arsenate employed in the fight against the boll weevil in the cotton states. Lead arsenate and Paris green (copper acetoarsenite) were used for arsenical sprays, and sodium arsenite was used as a weed killer and in sheep and cattle dips. Lead arsenate was used in poison sprays against pests that injure fruits and vegetables. Minor amounts of arsenic were also used in glass, in wood preservatives, in medicines, and in lead shot and copper alloys.

The use of arsenic in glass continues today, but at lower levels than in the 1960's and 1970's. The form of arsenic used has changed from powdered arsenic trioxide to the environmentally friendly liquid arsenic acid.

The major use for metallic arsenic is as a minor additive to lead used in lead-acid storage batteries. With the introduction of maintenance-free batteries in the 1970's, the use of arsenic in lead-acid batteries has declined. On the other hand, the use of arsenic in copper and/or brass alloys, and bearings (babbitt alloys) has remained an important small use.

Investigators discovered in the 1930's that organic forms of arsenic were useful as feed additives for chickens and poultry (10). Beginning in the 1950's, small amounts of high-purity arsenic metal were used in semiconductor electronic applications (11). These small applications are still used today.

Arsenic has been used in domestic agriculture as an ingredient in insecticides, herbicides, plant desiccants, and animal feed. Agricultural use peaked in the 1940's, when it accounted for more than 90% of arsenic use, but has since declined, both in tonnage and relative to other uses, until at present, it accounts for only about 15% of arsenic use (fig. 1). The decline in agricultural demand can be attributed to tighter environmental regulations imposed by the EPA on the use of inorganic arsenical chemicals. As

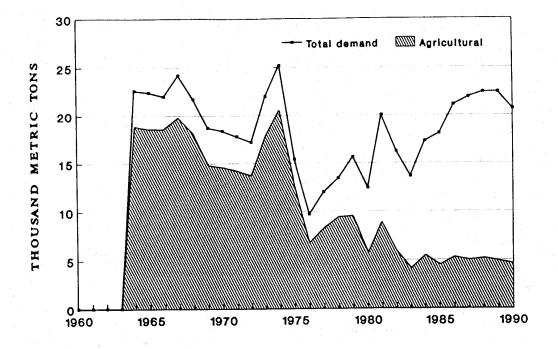
mentioned earlier, OSHA had determined in 1978 that inorganic arsenic is a human carcinogen.

In the late 1940's, effective new organic insecticides, such as dichloro-diphenyl-trichloro-ethane (DDT), became strong competitors of lead arsenate and calcium arsenate. Production of the two arsenates peaked in the early 1940's, and then began to decline slowly. However, they were still used extensively in the mid-1960's. However, as shown in figure 1, agricultural demand was down substantially by the mid-1970's. From about 1965 until 1992, arsenic acid was used to desiccate cotton plants in Texas and Oklahoma to remove leaves for mechanical cotton picking. Beginning about 1977, the organic arsenical herbicides monosodium methanearsonate (MSMA), disodium methanearsonate (DSMA), and cacodylic acid (dimethylarsinic acid) became popular. At present, there are no known producers of cacodylic acid, and the only remaining major agricultural use for arsenic is in the herbicides MSMA and DSMA. Small amounts of arsenic in the form of arsanilic acid are still used in feed additives.

In 1987, the EPA issued a preliminary decision to cancel the registration of most of the inorganic arsenicals used as nonwood pesticides. Included in the list were lead arsenate, calcium arsenate, sodium arsenate, and arsenic trioxide. The sole registrant of lead arsenate used as a plant growth regulator requested voluntary cancellation in 1987 and the registrant of products containing calcium arsenate requested cancellation in 1989 (12).

In 1991, the EPA announced its preliminary decision to cancel the registration of products containing arsenic acid used as a desiccant on cotton. The agency provided for a period of hearings before making its final decision on arsenic acid. In 1992, the two registrants for arsenic acid for use as a desiccant requested voluntary cancellation of their product (13).

There have been many different arsenic formulations used over the years for preserving wood. Crude arsenic has been used to treat fence posts. Wood was pressure-treated in the 1930's and before with zinc meta-arsenite



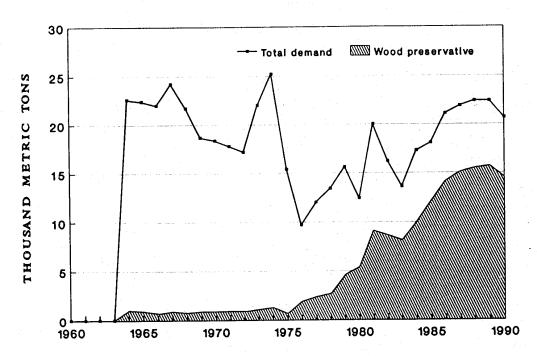


Figure 1.—U.S. arsenic demand, agriculture versus wood preservative.

(ZMA) (14). In the 1940's, 1950's, and 1960's, Wolman salts were popular, and to a lesser extent, ammoniacal copper arsenate (ACA) and fluor chrome arsenate phenol (FCAP). Beginning about 1972, chromated copper arsenate (CCA) compounds began to replace Wolman salts.

Wood preservative use did not appear to start growing rapidly until about 1975, as shown in figure 1. The use of arsenic in CCA wood preservatives has become the single most important application for arsenic today, accounting for about 80% of U.S. demand.

LOSSES FROM INDUSTRIAL AND COMMERCIAL PROCESSES

Arsenic is lost to the air, land, and water. These losses occur during the extractive metallurgical processing of nonferrous metals, during the manufacturing of arsenical products, and during the life and final disposal of the product. This paper attempts to estimate arsenic losses that occurred in 1989 in the domestic industry, as shown in figures 2 and 3. The year 1989 was chosen as a base year because final data were available for that year and because it was fairly close to the publication date of this paper; however, any recent year could have been chosen. In figure 3, extractive processing is separated from materials manufacturing and use to indicate that no arsenic is consumed from domestic sources—only from imported sources.

COPPER PROCESSING LOSSES

An attempt was made to calculate the arsenic losses from the U.S. copper processing industry (fig. 2) because it is the largest single source of emissions from the non-ferrous metals processing industry. In some cases, flue dusts containing lead, zinc, arsenic, and many other metals are processed in copper smelters. Detailed calculations for figure 2 are contained in the appendix. Many of the calculations were based on the assumption that there is approximately 13 lb of arsenic per short ton of copper reserves, or 6.5 kg of arsenic per mt of copper (15). Using the metric factor, the quantity of copper ore milled in 1989, and the mill-head grade of the ore, it was calculated

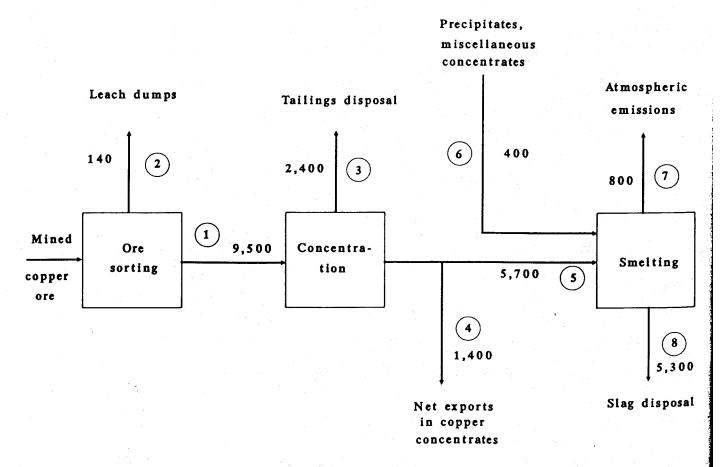


Figure 2.—Flow of arsenic in U.S. copper processing, 1989, in metric tons.

that about 9,500 mt of arsenic was contained in concentrated copper ore (fig. 2, location #1).

Similar calculations were performed to estimate the amount of arsenic going into leach dumps from copper mines (140 mt/yr) and the amount of arsenic contained in net exports of copper concentrates (1,400 mt/yr).

The amount of arsenic entering domestic smelters was calculated two different ways with fairly consistent results. In the first method, the arsenic content of concentrates was calculated by assuming 6.5 kg arsenic per metric ton of recoverable copper. The figure is adjusted for smelting and refining losses to arrive at the figure of 7,100 mt of arsenic contained in copper concentrates. Precipitates and miscellaneous ores and concentrates of copper added about 400 mt of arsenic to copper smelter inputs. After adjustment for arsenic contained in copper concentrate exports, the total amount of arsenic entering copper smelters was calculated to be 6,100 mt.

The second method used information from 1983 EPA estimates of the arsenic feed rate for 14 low-arsenic smelters (16). Asarco's high-arsenic smelter at Tacoma was

excluded from consideration because it was closed in 1985 and had processed principally imported high-arsenic concentrates whose importation ended with closure of the smelter. The EPA report states that the feed ore is a mixture of concentrates, precipitates, lead smelter byproducts. and smelter reverts. The arsenic content of the feed ore varies widely from smelter to smelter. The arsenic content of the now closed Asarco Tacoma smelter was as high as 4%, while the Tennessee Chemical Company-Copperhill plant had an arsenic content of as low as 0.0004%. Using the cumulative hourly feed rate for the 14 smelters and assuming 24 hr/day, 340 days/yr operation, the total arsenic feed for 14 low-arsenic smelters was calculated to be about 5,000 mt/yr. Using domestic anode production as the basis, the 1983 figure was factored up by 26% to account for increased 1989 smelter production. The resulting estimate of 6,300 mt of arsenic entering copper smelters correlated well with the 6,100 mt calculated previously. In the above calculation, it was assumed that although the number of smelters operating in 1989 was reduced, and that the concentrate feed patterns had changed, the overall arsenic content of domestic ores was unchanged.

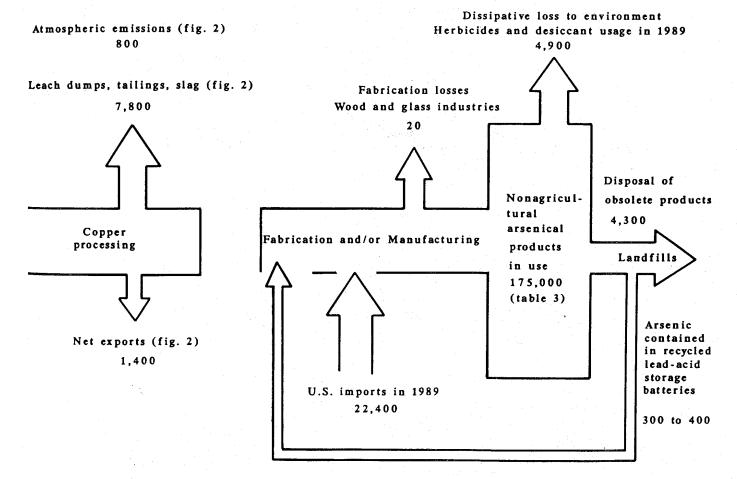


Figure 3.-U.S. materials flow for arsenic in 1989, in metric tons.

Arsenic going to tailings disposal (2,400 mt) from concentration was calculated as the difference of arsenic entering the copper concentrators less arsenic entering smelters, less net exports of arsenic.

Atmospheric emissions of arsenic from copper smelters were based on a 1983 Federal Register report stating that low-arsenic smelters with environmental controls in place had total arsenic emissions of 627 mt/yr (17). Factoring up production for copper from 1983 to 1989, arsenic emissions were estimated at about 800 mt in 1989. Subtracting the 800 mt emitted to the atmosphere from the total amount of arsenic entering the smelter indicates that 5,300 mt of arsenic was disposed of in slags.

FABRICATION INDUSTRY LOSSES

Small amounts of arsenic are emitted during the manufacture of arsenical products such as wood preservatives, herbicides and desiccants, glass products, and lead-acid batteries containing arsenic. However, these fabrication losses are believed to be very small in relation to copper processing losses.

About 70% of arsenic consumed in the United States in 1989 was used for wood preservatives. According to an EPA source, the losses of arsenic in the manufacture of wood preservatives in 1989 were minor, perhaps as low as 2 mt/yr (18). W. E. Davis and Associates estimated losses of arsenic from wood preservative manufacturing in 1968 to be less than 1 mt (19). Most arsenical wood waste comes from chemical residue remaining on the drip pad used in manufacturing pressure-treated wood. One wood preservative company estimated that there were about 450 wood treating plants in the United States, each

generating about 10 to 12 drums per year of waste, with a heavy metal content of 4% to 5%. The wood preservative companies pay \$300 to \$375 per drum to dispose of wastes (20).

Emissions of arsenic from glass manufacturing have dropped greatly over the years, from about 579 mt/yr in 1968 (21) to 18 mt/yr in the late 1980's. One of the reasons for the drop is that less arsenic is now used for glass decolorizing (900 mt in 1989 versus 1,900 mt in 1968).

In 1986, EPA published its final standards on arsenic emissions from glass manufacturing plants, which became effective on August 4, 1986 (22). The standard required new glass furnaces producing arsenic emissions greater than 0.4 mt/yr and existing furnaces producing arsenic emissions greater than 2.5 mt/yr to reduce emissions by 85%. As a result of this standard, and through the use of emissions control technology, arsenic emissions from all glass manufacturing declined from 32 mt/yr before the standard became effective to about 18 mt/yr after the standard became effective.

The fabrication losses shown in figure 3 include the losses from glass manufacturing (18 mt) and wood preservative manufacturing (2 mt) only. Losses from other industries, such as herbicide and desiccant production and lead-acid battery production are believed to be very small and would not significantly raise this figure.

In summary, the materials flow data shown in figure 3 for 1989 indicate that the U.S. copper processing industry releases about 10,000 mt/yr of arsenic, compared to about 9,220 mt/yr of arsenic released by the U.S. manufacturing and consuming industry.

RECYCLING

Arsenic used as a minor additive (about 0.01% to 0.5%) to lead in lead acid storage batteries is recovered and reused in new storage batteries, as shown in figure 3 (23). The amount is relatively small, probably 300 mt/yr to 400 mt/yr. This number is an estimate based on the 800 mt/yr of arsenic used in nonferrous alloys and electronics (table 2) and assuming some losses during recycling.

In producing pressure-treated wood, process water as well as rainwater draining from outdoor product storage yards is collected and reused. This "new scrap" remains in the manufacturing process. There is some hazardous solid waste containing arsenic and chromium generated during this process. Similarly, during the manufacture of gallium arsenide electronic devices, some new scrap is generated.

Gallium arsenide new scrap is recycled and high-purity metallic gallium and arsenic are produced from it (24).

Because of its relatively low price and hazardous nature, some companies have considered the disposal of arsenic as an alternative to recycling. One of the major problems for the nonferrous metals industry is stabilizing arsenic waste materials for long-term disposal. Much attention has been directed to the removal of arsenic from hydrometallurgical process solutions by precipitation with ferric iron. In the "Cashman Process," arsenic is fixed in a supposedly environmentally stable form as ferric arsenate (25). In a process developed by Newmont Mining, oxygen is added to gold ores to promote the formation of ferric arsenate (26). It is beyond the scope of this paper to discuss chemical stabilization processes, but a recent EPA-sponsored meeting on arsenic and mercury discussed this topic (27).

USEFUL LIFE OF ARSENICAL PRODUCTS

A materials flow for arsenic in 1989 (far right side of figure 3) was derived based on the useful life of arsenical products. The useful life of arsenical products varies greatly, depending on the product. Wood preservatives are generally guaranteed to prevent lumber from rotting for a period of about 30 years when used in the ground. Other products containing minor quantities of arsenic, such as glass and lead-acid batteries, probably have much shorter useful lives, perhaps from 5 years to 20 years. As a somewhat arbitrary average, 20 years was used as an average useful life on nonagricultural products. Based on the useful life of 20 years, the disposal of obsolete products in 1989 was set equal to the nonagricultural demand for arsenic in 1969 (1989 less 20 years). This is shown as being 4,300 mt in figure 3. It also appears in table 3 as the 1969 nonagricultural demand for arsenic. Table 3 shows cumulative (1969-89) nonagricultural demand for arsenic as 175,000 mt. This is shown in figure 3 as total nonagricultural arsenical products in use over the 20-year life.

Agricultural products containing arsenic have short useful lives of less than 1 year and are therefore considered dissipative. These products include arsenic contained in herbicides and desiccants used in cotton farming and for controlling the growth of weeds. The consumption of arsenic in dissipative uses in 1989 is shown as 4,900 mt in figure 3. This figure is shown in table 3 as the agricultural demand for arsenic in 1989.

After arsenic has served it useful life as a wood preservative in a wood deck or fence post, the wood could be removed and discarded in a landfill. Another possibility is that the wood would remain in place, eventually rot, and the arsenic would be absorbed into the soil.

Table 3.—Arsenical products in use in 1989

(Metric tons)

Year	Total demand	Agricultural demand	Nonagricultura demand		
1969	20,600	16,300	4,300		
1970	20,300	16,100	4,200		
1971	19,640	15,600	4,040		
1972	18,970	15,100	3,870		
1973	22,000	17,900	4,100		
1974	25,200	20,600	4,600		
1975	15,400	12,700	2,700		
1976	9,700	6,800	2,900		
1977	12,000	8,300	3,700		
1978	13,400	9,400	4,000		
1979	15,600	9,500	6,100		
1980	12,400	5,700	6,700		
1981	20,000	8,900	11,100		
1982	16,200	5,900	10,300		
1983	13,600	4,100	9,500		
1984	17,300	5,500	11,800		
1985	18,100	4,500	13,600		
1986	21,100	5,300	15,800		
1987	21,900	5,000	16,900		
1988	22,300	5,100	17,200		
1989	22,300	4,900	17,400		
Cumulative	total (round	ed)	175,000		

Sources: Arsenic. Chapters in Mineral Facts and Problems, 1975, 1980, and 1985 Editions. Bullines Bulletins 667, 671, 675. Mineral Industry Surveys, Annual Review, Arsenic in 1989-91.

CONCLUSIONS

For 60 years (1920-80), most arsenic in the United States was consumed by the agricultural industry for use in manufacturing insecticides, herbicides, and cotton desiccants. After 1980, a shift occurred, and wood preservation became the most important application for arsenic. Government regulation due to the toxic nature of arsenic and concern for worker safety has played a role in shaping both the uses and the domestic production of arsenic. As a result, domestic production and agricultural uses for arsenic have been sharply curtailed.

The major source of domestic arsenic emissions in 1989 was from the copper processing industry, which discarded about 7,800 mt/yr of arsenic in leach dumps, tailings, and

slag, liberated another 800 mt/yr to the atmosphere, and exported 1,400 mt/yr in copper concentrates. On the consumption side, fabrication industry losses from the wood and glass industries was a minor 20 mt/yr. Dissipative loss to the environment from herbicide and desiccant usage was 4,900 mt/yr. Based on a useful life of 20 years, the disposal of obsolete arsenical products added 4,300 mt/yr of arsenic to the environment.

More data should be collected on the ultimate disposition of arsenical products. For example, information is needed on the disposition of treated wood after it has served its useful life. Another topic for study is a detailed analysis of industry losses during fabrication.

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APPENDIX.—CALCULATIONS FOR FIGURE 2

Location #1

Copper ore concentrated in 1989 was 230,526,000 mt 230,526,000

- × .00636 (mill head grade)
- × 6.5 kg arsenic/mt copper

9,530,000 kg arsenic use 9,500 mt

Location #2

6,736,000 mt ore placed on leach dumps in 1989

- x .00325 (estimated copper content of leached ore)
- × 6.5

142,000 kg arsenic use 140 mt

Location #4

Copper concentrates showed net exports in 1989 266,831 mt exports

- 46,516 imports

220,315 net exports

× 6.5

1,432,000 kg arsenic use 1,400 mt

Location #5

1,126,382 mt copper concentrate produced in 1989

7,321,483 kg

7,321 mt

/ .97 smelting refining losses for recoverable copper

7,100

- 1,400 arsenic loss from net exports (location #4)

5,700 mt arsenic

Alternative for calculating arsenic feed to smelter Calculated from April 1983, EPA-450-83-009, Table 2-3

Total arsenic feed rate for 14 low arsenic

smelters
Assume 24 hr/day operation
Assume 340 days/yr

Total low arsenic feed in 1983

618 kg/hr

× 24

× 340

5,000 mt

Factor to 1989 1989 domestic anode/1983 domestic anode 1,120 / 888 = 1,26

Low arsenic feed in 1983

5,000 mt × 1.26 6,300 mt arsenic

Location #3

location #1 less location #5 less location #4

9,500

- 5,700

- 1,400

2,400 mt arsenic

Location #6

Precipitates and miscellaneous ores and concentrates of copper in 1989

59,000 mt

× 6.5

384,000 kg arsenic use 400 mt

Location #7

Federal Register, July 20, 1983, p. 33122

Low arsenic smelters with controls have total emissions of 627 mt/yr.

627

× 1.26 (factored up production from 1983 to 1989)

790 mt arsenic use 800 mt

Location #8

Slag disposal (location #5 plus location #6 less location #7)

5,700

+ 400

- 800

5,300